Abstract. These notes provide an introduction to:
- Methods for the expression of isotopic abundances,
- Isotopic mass balances, and
- Isotope effects and their consequences in open and closed systems.

Notation. Absolute abundances of isotopes are commonly reported in terms of atom percent. For example, atom percent $\text{^{13}C} = \frac{[\text{^{13}C}/(\text{^{12}C} + \text{^{13}C})]}{100}$ (1)

A closely related term is the fractional abundance
fractional abundance of $\text{^{13}C} \equiv \frac{\text{^{13}F}}{\text{^{12}C} + \text{^{13}C}}$ (2)

$\text{^{13}F} = \frac{\text{^{13}C}}{(\text{^{12}C} + \text{^{13}C})}$ (2)

These variables deserve attention because they provide the only basis for perfectly accurate mass balances.

Isotope ratios are also measures of the absolute abundance of isotopes; they are usually arranged so that the more abundant isotope appears in the denominator

"carbon isotope ratio" = $\frac{\text{^{13}C}}{\text{^{12}C}}$ (3)

For elements with only two stable nuclides (H, C, and N, for example), the relationship between fractional abundances and isotope ratios is straightforward

$\frac{^{13}R}{1 + ^{13}F}$ (4)

$\delta^{13} = \frac{^{13}R}{1 + ^{13}R}$ (5)

Equations 4 and 5 also introduce a style of notation. In mathematical expressions dealing with isotopes, it is convenient to follow the chemical convention and to use left superscripts to designate the isotope of interest, thus avoiding confusion with exponents and retaining the option of defining subscripts. Here, for example, we have written $^{13}F$ rather than $F_{13}$ or $F^{13}$. Parallel version of equations 4 and 5 pertain to multi-isotopic elements. In the case of oxygen, for example,

$^{18}R = \frac{^{18}F}{1 - ^{18}F}$ (4a)

$^{18}F = \frac{^{18}R}{1 + ^{18}R}$ (5a)

Natural variations of isotopic abundances. The isotopes of any element participate in the same chemical reactions. Rates of reaction and transport, however, depend on nuclidic mass, and isotopic substitutions subtly affect the partitioning of energy within molecules. These deviations from perfect chemical equivalence are termed isotope effects. As a result of such effects, the natural abundances of the stable isotopes of practically all elements involved in low-temperature geochemical ($< 200^\circ C$) and biological processes are not precisely constant. Taking carbon as an example, the range of interest is roughly $0.00998 \leq ^{13}F \leq 0.01121$. Within that range, differences as small as 0.00001 can provide information about the source of the carbon and about processes in which the carbon has participated.

The delta notation. Because the interesting isotopic differences between natural samples usually occur at and beyond the third significant figure of the isotope ratio, it has become conventional to express isotopic abundances using a differential notation. To provide a concrete example, it is far easier to say – and to remember – that the isotope ratios of samples A and B differ by one part per thousand than to say that sample A has 0.3663 \%^{15}N and sample B has 0.3659 \%^{15}N. The notation that provides this advantage is indicated in general form below [this means of describing isotopic abundances was first used by Urey (1948) in an address to the American Association for the Advancement of Science, and first formally defined by McKinney et al. (1950)]

$\delta^{XSTD} = \frac{A_{\text{Sample}}}{A_{\text{STD}}} - 1$ (6)

Where $\delta$ expresses the abundance of isotope A of element X in a sample relative to the abundance of that same isotope in an arbitrarily designated reference material, or isotopic standard. For hydrogen and oxygen, that reference material was initially Standard Mean Ocean Water (SMOW). For carbon, it was initially a particular calcareous fossil, the PeeDee Belemnite (PDB; the same standard served for oxygen isotopes in carbonate minerals). For nitrogen it is air (AIR). Supplies of PDB and of the water that defined SMOW have been exhausted. Practical scales of isotopic abundance are now defined in terms of surrogate standards distributed by the International Atomic Energy Authority’s laboratories in Vienna. Accordingly, modern reports often present values of $\delta_{\text{SMOW}}$ and $\delta_{\text{PDB}}$. These are equal to values of $\delta_{\text{SMOW}}$ and $\delta_{\text{PDB}}$.

The original definition of $\delta$ (McKinney et al., 1950) multiplied the right-hand side of equation 6 by 1000. Isotopic variations were thus expressed in parts per thousand and assigned the symbol ‰ (permil, from the Latin per mille by analogy with per centum, percent). Equa-
tions based on that definition are often littered with factors of 1000 and 0.001. To avoid this, it is more convenient to define \( \delta \) as in equation 6. According to this view (represented, for example, by Farquhar et al., 1989 and Mook, 2000), the \( \% \) symbol implies the factor of 100 and we can equivalently write either \( \delta = -25\% \) or \( \delta = -0.025 \).

To avoid clutter in mathematical expressions, symbols for \( \delta \) should always be simplified. For example, \( \delta_i \) can represent \( \delta^{13}C_{\text{PDB}}( \text{HCO}_3^-) \). If multiple elements and isotopes are being discussed, variables like \( ^{13}\delta \) and \( ^{15}\delta \) are explicit and allow use of right subscripts for designating chemical species.

**Mass-Balance Calculations.** Examples include (i) the calculation of isotopic abundances in pools derived by the combination of isotopically differing materials, (ii) isotope-dilution analyses, and (iii) the correction of experimental results for the effects of blanks. A single, master equation is relevant in all of these cases. Its conceptual base is rudimentary: Heavy isotopes in product = Heavy isotopes in precursors. In mathematical terms:

\[
m_S F_x = m_1 F_1 + m_2 F_2 + ... \tag{7}
\]

where the \( m \) terms represent molar quantities of the element of interest and the \( F \) terms represent fractional isotopic abundances. The subscript \( \Sigma \) refers to total sample derived by combination of subsamples 1, 2, ..., etc. The same equation can be written in approximate form by replacing the \( F \)s with \( \delta \)s. Then, for any combination of isotopically distinct materials:

\[
\delta_x = \Sigma m_i \delta_i / \Sigma m_i \tag{8}
\]

Equation 8, though not exact, will serve in almost all calculations dealing with natural isotopic abundances. The errors can be determined by comparing the results obtained using equations 7 and 8. Taking a two-component mixture as the simplest test case, errors are found to be largest when \( \delta_x \) differs maximally from both \( \delta_1 \) and \( \delta_2 \), i.e., when \( m_1 = m_2 \). For this worst case, the error is given by

\[
\delta_x - \delta_{x*} = (R_{\text{STD}})[(\delta_1 - \delta_2)/2] \tag{9}
\]

Where \( \delta_x \) is the result obtained from eq. 8; \( \delta_{x*} \) is the exact result, obtained by converting \( \delta_1 \) and \( \delta_2 \) to fractional abundances, applying eq. 7, and converting the result to a \( \delta \) value; and \( R_{\text{STD}} \) is the isotopic ratio in the standard that establishes the zero point for the \( \delta \) scale used in the calculation. The errors are always positive. They are only weakly dependent on the absolute value of \( \delta_1 \) or \( \delta_2 \) and become smaller than the result of eq. 9 as \( \delta > 0 \). If \( R_{\text{STD}} \) is low, as for \( ^2\text{H} (R_{\text{VSMOW}} = 1.5 \times 10^{-4}) \), the errors are less than 0.04\% for any \( |\delta_1 - \delta_2| \leq 1000\% \).

For carbon \( (^{13}R_{\text{PDB}} = 0.011) \), errors are less than 0.03\% for any \( |\delta_1 - \delta_2| \leq 100\% \).

The excellent accuracy of eq. 8 does not mean that all simple calculations based on \( \delta \) will be similarly accurate. As noted in a following section, particular care is required in the calculation and expression of isotopic fractionations. And, when isotopically labeled materials are present, calculations based on \( \delta \) should be avoided in favor of eq. 7.

**Isotope dilution.** In isotope-dilution analyses, an isotopic spike is added to a sample and the mixture is then analyzed. The original “sample” might be a material from which a representative subsample could be obtained but which could not be quantitatively isolated (say, total body water). For the mixture \( \Sigma \) of the sample \( x \) and the spike \( k \), we can write:

\[
(m_x + m_k) F_{\Sigma} = m_x F_x + m_k F_k \tag{10}
\]

Rearrangement yields an expression for \( m_x \) (e.g., moles of total body water) in terms of \( m_k \), the size of the spike, and measurable isotopic abundances:

\[
m_x = m_k (F_k - F_{\Sigma}) / (F_{\Sigma} - F_x) \tag{11}
\]

Since we are dealing here with a mass balance, \( \delta \) can be substituted for \( F \) unless heavily labeled spikes are involved.

**Blank corrections.** When a sample has been contaminated during its preparation by contributions from an analytical blank, the isotopic abundance actually determined during the mass spectrometric measurement is that of the sample plus the blank. Using \( \Sigma \) to represent the sample prepared for mass spectroscopic analysis and \( x \) and \( b \) to represent the sample and blank, we can write

\[
m_{\Sigma} \delta_x = m_x \delta_x + m_b \delta_b \tag{12}
\]

Substituting \( m_x = m_\Sigma - m_b \) and rearranging yields

\[
\delta_x = \delta_{\Sigma} - m_b (\delta_x - \delta_{\Sigma}) / m_{\Sigma} \tag{13}
\]

an equation of the form \( y = a + bx \). If multiple analyses are obtained, plotting \( \delta_x \) vs. \( 1/m_\Sigma \) will yield the accurate (i.e., blank-corrected) value of \( \delta_x \) as the intercept.

**Calculations related to isotope effects**

An isotope effect is a physical phenomenon. It cannot be measured directly, but its consequences—a partial separation of the isotopes, a *fractionation*—can sometimes be observed. This relationship is indicated schematically in Figure 1.

**Fractionation.** Two conditions must be met before an isotope effect can result in fractionation. First, the system in which the isotope effect is occurring must be arranged so that an isotopic separation *can* occur. If a reactant is transformed completely to yield some product, an isotopic separation which might have been
visible at some intermediate point will not be observable because the isotopic composition of the product must eventually duplicate that of the reactant. Second, since isotope effects are small enough that they don’t upset blanket statements about chemical properties, the techniques of measurement must be precise enough to detect very small isotopic differences.

Observed fractionations are proportional to the magnitudes of the associated isotope effects. Examples of equilibrium and kinetic isotope effects are shown in Figure 2. As indicated, the magnitude of an equilibrium isotope effect can be represented by an equilibrium constant. In this example, the reactants and products are chemically identical (carbon dioxide and bicarbonate in each case). However, due to the isotope effect, the equilibrium constant is not exactly 1. There is, however, a problem with the use of equilibrium constants to quantify isotope effects. An equilibrium constant always pertains to a specific chemical reaction, and, for any particular isotopic exchange, the reaction can be formulated in various ways, for example:

\[ \text{H}_2^{18}\text{O} + 1/3 \text{CaC}_1^6\text{O}_3 \rightleftharpoons \text{H}_2^{16}\text{O} + 1/3 \text{CaC}_1^8\text{O}_3 \]  

vs.

\[ \text{H}_2^{18}\text{O} + \text{CaC}_1^6\text{O}_3 \rightleftharpoons \text{H}_2^{16}\text{O} + \text{CaC}_1^8\text{O}_1^6\text{O}_2 \]  

To avoid such ambiguities, EIEs are more commonly described in terms of fractionation factors.

A fractionation factor is always a ratio of isotope ratios. For the example in Figure 2, the fractionation factor would be:

\[ \alpha_{\text{HCO}_3/\text{CO}_2} = \frac{^{13}\text{C}}{^{12}\text{C}}_{\text{HCO}_3} / \frac{^{13}\text{C}}{^{12}\text{C}}_{\text{CO}_2} \]  

A more compact and typical representation would be

\[ \frac{^{13}\text{C}_{/^{12}\text{C}}_{\text{HCO}_3}}{^{13}\text{C}_{/^{12}\text{C}}_{\text{CO}_2}} = \alpha \]  

where \( \alpha \) is the fractionation factor for the isotope ratio of interest.

Reversibility and systems. Given a fractionation factor, isotopic compositions of reactants and products can usually be calculated once two questions have been answered:

1. Is the reaction reversible?
2. Is the system open or closed?
An open system is one in which both matter and energy are exchanged with the surroundings. In contrast, only energy crosses the boundaries of a closed system.

Reversibility and openness vs. closure are key concepts. Each is formally crisp, but authors often sew confusion. If a system is described as “partially closed,” readers should be on guard. If the description means that only some elements can cross the boundaries of the system, the concept might be helpful. If partial closure instead refers to impeded transport of materials into and out of the system, the concept is invalid and likely to cause problems.

Openness covers a range of possibilities. Some open systems are at steady state, with inputs and outputs balanced so that the inventory of material remains constant. In others, there are no inputs but products are treated simply, others require specific models.

Reversible reaction, closed system. In such a system, (1) the isotopic difference between products and reactants will be controlled by the fractionation factor and (2) mass balance will prevail.

To develop a quantitative treatment, we will consider an equilibrium between substances A and B,

\[ \text{A ⇌ B} \]  

(19)

The isotopic relationship between these materials is defined in terms of a fractionation factor:

\[ \alpha_{\text{A/B}} = \frac{R_{\text{A}}}{R_{\text{B}}} = \frac{\delta_{\text{A}} + 1}{\delta_{\text{B}} + 1} \]  

(20)

where the Rs are isotope ratios and the \( \delta \) values are the corresponding \( \delta \) values on any scale of abundances (the same scale must be used for both the product and the reactant). The requirement that the inventory of materials remain constant can be expressed inexactly, but with good accuracy, in terms of a mass-balance equation:

\[ \delta_{\text{Σ}} = f_{\text{B}} \delta_{\text{B}} + (1 - f_{\text{B}}) \delta_{\text{A}} \]  

(21)

where \( \delta_{\text{Σ}} \) refers to the weighted-average isotopic composition of all of the material involved in the equilibrium (for equation 14 or 15, it would refer to all of the oxygen in the system) and \( f_{\text{B}} \) refers to the fraction of that material which is in the form of B. By definition, the fraction of material in the form of A is \( 1 - f_{\text{B}} \).

Rearrangement of equation 20 yields:

\[ \delta_{\text{A}} = \alpha_{\text{A/B}} \delta_{\text{B}} + (\alpha_{\text{A/B}} - 1) \]  

(22)

The second term on the right-hand side of this equation is commonly denoted by a special symbol:

\[ \alpha - 1 \equiv \varepsilon \]  

(23)

Equation 22 then becomes:

\[ \delta_{\text{A}} = \alpha_{\text{A/B}} \delta_{\text{B}} + \varepsilon_{\text{A/B}} \]  

(24)

(Like \( \delta, \varepsilon \) is often expressed in parts per thousand. For example, if \( \alpha = 1.0077 \), then \( \varepsilon = 0.0077 \) or 7.7‰. Dimensional analysis reliably indicates the form required in any calculation. In equations 24-29, all terms could be dimensionless or could be expressed in permil units. The dimensionless form is required in equation 20, where \( \delta \) is added to a dimensionless constant, in equations 39 and 40, where use of permil units would unbalance the equations, and in equations 41 and 42, where \( \delta \) and/or \( \varepsilon \) appear as exponents or in the arguments of transcendental functions.)

Substituting for \( \delta_{\text{A}} \) in equation 21, we obtain

\[ \delta_{\text{Σ}} = f_{\text{B}} \delta_{\text{B}} + (1 - f_{\text{B}})(\alpha_{\text{A/B}} \delta_{\text{B}} + \varepsilon_{\text{A/B}}) \]  

(25)

Solving for \( \delta_{\text{B}} \), we obtain an expression which allows calculation of \( \delta_{\text{B}} \) as a function of \( f_{\text{B}} \), given \( \alpha_{\text{A/B}} \) and \( \delta_{\text{Σ}} \):

\[ \delta_{\text{B}} = \frac{\delta_{\text{Σ}} - (1 - f_{\text{B}}) \varepsilon_{\text{A/B}}}{\alpha_{\text{A/B}}(1 - f_{\text{B}}) + f_{\text{B}}} \]  

(26)

If equation 24 is rearranged to express \( \delta_{\text{B}} \) in terms of \( \delta_{\text{A}} \), \( \alpha_{\text{A/B}} \), and \( \varepsilon_{\text{A/B}} \), and the result is substituted for \( \delta_{\text{B}} \) in equation 21, we obtain a complementary expression for \( \delta_{\text{A}} \):

\[ \delta_{\text{A}} = \frac{\alpha_{\text{A/B}} \delta_{\text{Σ}} + f_{\text{B}} \varepsilon_{\text{A/B}}}{\alpha_{\text{A/B}}(1 - f_{\text{B}}) + f_{\text{B}}} \]  

(27)

Equations 26 and 27 are generally applicable but rarely employed because adoption of the approximation \( \alpha_{\text{A/B}} = 1 \) yields far simpler results, namely:

\[ \delta_{\text{A}} = \delta_{\text{Σ}} + f_{\text{B}} \varepsilon_{\text{A/B}} \]  

(28)

and

\[ \delta_{\text{B}} = \delta_{\text{Σ}} - (1 - f_{\text{B}}) \varepsilon_{\text{A/B}} \]  

(29)

Graphs depicting these relationships can be constructed very easily. An example is shown in Figure 3. For \( f_{\text{B}} = 1 \) we must have \( \delta_{\text{B}} = \delta_{\text{Σ}} \) and for \( f_{\text{B}} = 0 \) we must have \( \delta_{\text{A}} = \delta_{\text{Σ}} \). As shown in Figure 3, the intercepts for the other ends of the lines representing \( \delta_{\text{A}} \) and \( \delta_{\text{B}} \) will be \( \delta_{\text{Σ}} \pm \varepsilon_{\text{A/B}} \). If \( \alpha_{\text{A/B}} < 1 \), \( \varepsilon_{\text{A/B}} \) will be negative and A will be isotopically depleted relative to B. The lines representing \( \delta_{\text{A}} \) and \( \delta_{\text{B}} \) will slope upward as \( f_{\text{B}} \) → 0. If \( \alpha_{\text{A/B}} > 1 \) then A would be enriched relative to B and the lines would slope downward.

There are two circumstances in which the approximation leading to equations 28 and 29 (i.e., \( \alpha_{\text{A/B}} = 1 \)) must be examined. The first involves highly precise studies and the second almost any hydrogen-isotopic fractionations. As an example of the first case, Figure 4 compares the results of equations 26 and 27 to those of 28 and 29 for a system with \( \alpha_{\text{A/B}} = 1.0412 \). This is, in fact, the fractionation factor for the exchange of oxygen
between water and gas-phase carbon dioxide at 25°C (where A is CO₂ and B is H₂O). The solid and dotted lines in the larger graph represent the more accurate and the approximate results, respectively. The lines in the smaller graph in Figure 4 represent the errors, which significantly exceed the precision of measurement (which is typically better than 0.1‰).

For many hydrogen-isotopic fractionations, $\alpha$ differs from 1.0 by more than 10%. In such cases, the approximation fails and a magnifying lens is not needed to see the difference between the accurate and the approximate results. An example is shown in Figure 5.

Irreversible reaction, closed system. The goal is to determine the isotopic relationship between the reactants and products over the course of the reaction, starting with only reactants and ending with a 100% yield of products. We’ll consider the general reaction $R \rightarrow P$ (Reactants $\rightarrow$ Products). If the rate is sensitive to isotopic substitution, we’ll have $\alpha_{P/R} \neq 1$, where

$$\alpha_{P/R} = R_{P,i}/R_R$$  \hspace{1cm} (30)

In this equation, $\alpha_{P/R}$ is the fractionation factor, $R_{P,i}$ is the isotope ratio (e.g., $^{13}$C/$^{12}$C) of an increment of product and $R_R$ is the isotope ratio of the reactant at the same time. Following the approach of Mariotti et al. (1981) and expressing $R_{P,i}$ in terms of differential quantities, we can write

$$f_B$$

$\delta_{\Sigma} - \varepsilon_{A/B}$

$\delta_{\Sigma} + \varepsilon_{A/B}$

$\delta_B$

$\delta_A$

Figure 3. General form of a diagram depicting isotopic compositions of species related by a reversible chemical reaction acting in a closed system.

$\alpha_{A/B} = 1.0412$

$\delta_{\Sigma} = 0$

Error, ‰

$\delta_B$

$\delta_A$

Figure 4. Graphs showing results of both accurate and approximate calculations of isotopic compositions of reactants and products of a reversible reaction in a closed system. The dotted lines in the upper graph are drawn as indicated in Figure 3 and by equations 28 and 29. The solid lines are based on equations 26 and 27. The differences between these treatments are shown in the smaller graph.

$$\alpha_{P/R} = \frac{dm_{IP}}{dm_{IR}} \left/ \frac{m_{hR}}{m_{lR}} \right.$$

(31)

where the $m$s represent molar quantities and the subscripts designate the heavy and light isotopic species of the Product and Reactant. In absence of side reactions, $dm_{hP} = -dm_{hR}$ and $dm_{lP} = -dm_{lR}$. Employing these substitutions, the equation can be expressed entirely in terms of quantities of reactant:
Separating variables and integrating from initial conditions to any arbitrary point in the reaction, we obtain

\[
\frac{m_{IR}}{m_{IR,0}} \left( \frac{m_{hR}}{m_{IR,0} + 1} \right) = \frac{m_{IR} (R_R + 1)}{m_{IR,0} (R_{R,0} + 1)} = f \tag{35}
\]

Which yields

\[
\frac{m_{IR}}{m_{IR,0}} = f \cdot \frac{1 + R_{R,0}}{1 + R_R} \tag{36}
\]

Similar rearrangements yield

\[
\frac{m_{hR}}{m_{hR,0}} = f \cdot \frac{R_R}{R_{R,0}} \cdot \frac{1 + R_{R,0}}{1 + R_R} \tag{37}
\]

So that equation 33 becomes

\[
\alpha_{P/R} \ln \left( f \cdot \frac{1 + R_{R,0}}{1 + R_R} \right) = \ln \left( f \cdot \frac{1 + R_{R,0}}{1 + R_R} \frac{R_R}{R_{R,0}} \right) \tag{38}
\]

Which can be rearranged to yield

\[
\epsilon_{P/R} \ln f = \ln \frac{R_R}{R_{R,0}} \tag{39}
\]

an expression which duplicates exactly equation V.17 in the rigorous treatment by Bigeleisen and Wolfsburg (1958). Without approximation, this equation relates the isotopic composition of the residual reactant \(R_R\) to that of the initial reactant \(R_{R,0}\), to the isotope effect \(\alpha_{P/R}\), and to \(f\), the extent of reaction.

If the abundance of the rare isotope is low, the coefficient for \(f\cdot(1 + R_{R,0})/(1 + R_R)\), is almost exactly 1. In that case, equation 39 becomes

\[
\epsilon_{P/R} \ln f = \ln \frac{R_R}{R_{R,0}} \tag{40}
\]

Because quantities with equal logarithms must themselves be equal, we can write

\[
f^{\epsilon_{P/R}} = \frac{R_R}{R_{R,0}} \tag{41}
\]

Equation 41 is often presented as “The Rayleigh Equation.” It was developed by Lord Rayleigh (John William Strutt, 1842-1919) in his treatment of the distillation of liquid air and was exploited by Sir William Ramsey (1852-1916) in his isolation first of argon and then of krypton, and xenon. The ratios in these cases were not isotopic. The concept of isotopes was introduced by Frederick Soddy (1877-1956) in 1913, long after Strutt and Ramsey had been awarded the Nobel Prizes in physics and chemistry, respectively, in 1904. Instead, the ratios in Rayleigh’s conception pertained to the abun-

\[
\alpha_{A/B} = 0.800
\]

\[
\delta_{c} = +100\%
\]

\[
\delta_{c,0} = 0
\]

\[
f = \frac{m_{hR}}{m_{hR,0} + m_{IR,0}} = \frac{m_{hR}}{m_{IR,0} + m_{IR,0}}
\]

Avoiding approximations introduced by Mariotti et al. (1981), we rearrange this equation to yield exact substitutions for the arguments of the logarithms in equation 33. For example:
dances of Ar, Ne, Kr, and Xe relative to N$_2$ and, as the distillation proceeded, relative to each other.

Figure 6 indicates values of $R_R$ that are in accordance with equation 41 (viz., the line marked $R_R$ on the horizontal axis, “yield of P” = 1 − $f$). If the objective is to use observed values of $\delta_R$ and/or $\delta_R$ in order to evaluate $\epsilon_{P/R}$, a linear form is often desirable. One which is linear and exact is provided by equation 39.

Values of $\delta_R$ must be converted to isotope ratios and the initial composition of the reactant must be known. Regression of $\ln(\frac{R_R}{R_{R,0}})$ on $\ln[f(1 + R_{R,0})/(1 + R_R)]$ will then yield $\epsilon_{P/R}$ as the slope.

By use of approximations, Mariotti et al. (1981) developed less cumbersome forms. The first is derived by rewriting equation 40 with the argument of the logarithm in the delta notation. Rearrangement then yields

$$\ln(\delta_R + 1) = \ln(\delta_{R,0} + 1) + \epsilon_{P/R} \ln f \quad (42)$$

This is an expression of the form $y = a + bx$. Regression of $\ln(\delta_R + 1)$ on $\ln f$ yields a straight line with slope $\epsilon_{P/R}$.

A second form is very widely applied. Noting that $\ln[(1 + u)/(1 + v)] \equiv u - v$ when $u$ and $v$ are small relative to 1, Mariotti et al. (1981) simplified eq. 42 to obtain

$$\delta_R = \delta_{R,0} + \epsilon_{P/R} \ln f \quad (43)$$

This is also an expression of the form $y = a + bx$. Moreover, it is an equation in which all terms can be expressed in permil units. Regression of $\delta_R$ on $\ln f$ will yield $\epsilon_{P/R}$ as the slope and $\delta_{R,0}$, which need not be known independently, as the intercept.

The approximations leading to equations 42 and 43 can lead to systematic errors. These are examined in Figure 7, which is based on values of $\delta$ and $\epsilon$ that are typical for $^{13}$C. Equation 42 is based on the approximation that $m_R/m_{R,0}$ does not differ significantly from $m_R/m_{R,0}$ (cf. eq. 34). This is evidently much more satisfactory than the approximation leading to equation 43, which produces systematic errors that are larger than analytical uncertainties for values of $f < 0.4$. Equation 43 should never be used in hydrogen-isotopic calculations, for which the approximation $u \approx v \ll 1$ is completely invalid.

Equations 39-43 pertain to values of $\delta_R$, the isotopic composition of the reactant available within the closed system. Figure 6 also shows lines marked P and $P'$ representing respectively the isotopic compositions of the pooled product and of the product forming at any point in time. The relationship between R and $P'$ always follows directly from the fractionation factor:
As noted in Figure 6, this leads to a constant isotopic difference (designated $B$ in the Figure) between $R$ and $P'$. Initially, both the pooled product, $P$, and $P'$ are depleted relative to $R$ by the same amount. As the reaction proceeds, the isotopic composition of $P$ steadily approaches that of the initial reactant. The functional relationship can be derived from a mass balance:

$$m_R\delta_R,0 = m_R\delta_R + m_P\delta_P \quad (45)$$

substituting $m_R/m_R,0 = f$ and $m_P/m_R,0 = 1 - f$, combination of equations 43 and 45 yields

$$\delta_P = \delta_R,0 - \frac{f}{(1 - f)}\epsilon_{P/R} \ln f \quad (46)$$

an expression which shows that the regression of $\delta_P$ on $\frac{f}{(1 - f)}\ln f$ will yield $\epsilon_{P/R}$ as the slope.

Systematic errors associated with equation 46, summarized graphically in Figure 8, are smaller than those in equation 43 (note the differing vertical scales in Figs. 7 and 8).

In practical studies of isotope effects, the most vexing problem is usually not whether to accept approximations but instead how to combine observations from multiple experiments. The problem has been explored systematically and very helpfully by Scott et al. (2004), who have, in addition, concluded that calculations based on equation 42 are most likely to provide the smallest uncertainties. Notably, they recommend regression of $\ln f$ on $\ln(\delta_R + 1)$, thus necessitating transformation of the regression constants in order to obtain a value for $\epsilon_{P/R}$. Although both $f$ and $\delta_R$ are subject to error, use of a Model I linear regression, and thus assuming that errors in $\delta_R$ are small in comparison to those in $f$, is recommended.

**Figure 9.** Schematic view of an open system which is supplied with reactant $R$ and from which products $P$ and $Q$ are withdrawn.

**Reversible reaction, open system (product lost).** Atmospheric moisture provides the classical example of systems of this kind. Water vapor condenses to form a liquid or solid which precipitates from the system. Vapor pressure isotope effects lead to fractionation of the isotopes of both H and O. The process of condensation is reversible, but the evolution of isotopic compositions is described by the same equations introduced above to describe fractionations caused by an irreversible reaction in a closed system. The heavy isotopes accumulate in the condensed phases. Consequently, the residual reactant (the moisture vapor remaining in the atmosphere) is described by increasingly negative values of $\delta_R$. The curves describing the isotopic compositions have the same shape as those in Figure 6, but bend downward rather than upward.

**Reversible or irreversible reaction, open system at steady state.** A schematic view of a system of this kind is shown in Figure 9. A reactant, $R$, flows steadily into a stirred reaction chamber. Products $P$ and $Q$ flow from the chamber. The amount of material in the reaction chamber is constant and, therefore,

$$J_R = J_P + J_Q \quad (47)$$

Where $J$ is the flux of material, moles/unit time.

The relevant fractionation factors are

$$\alpha_{P/R} = \frac{R_P'}{R_R} = \frac{\delta_P' + 1}{\delta_R + 1} \quad (48)$$

and

$$\alpha_{Q/R} = \frac{R_Q}{R_R} = \frac{\delta_Q + 1}{\delta_R + 1} \quad (49)$$

It doesn’t matter whether these fractionations result from reversible equilibria or from kinetically limited processes that operate consistently because residence times within the reactor are constant. As a result of these processes, the isotopic difference between $P$ and $Q$ can also be described by a fractionation factor.
Given these conditions, isotopic fractionations for any system of this kind are described by equations 26 and 27 (or by eq. 28 and 29 if $a \approx 1$), with $P$ and $Q$ equivalent to $A$ and $B$ and $R$ equivalent to the material designated by $\Sigma$. The value of $f_B$ is given by $J_Q/J_R$.

Systems of this kind range widely in size. The treatment just described is conventional in models of the global carbon cycle, in which the reaction chamber is the atmosphere + hydrosphere + biosphere, $R$ is recycling carbon entering the system in the form of CO$_2$, and $P$ and $Q$ are organic and carbonate carbon being buried in sediments. The value of $\alpha_{R/Q}$, the fractionation between CO$_2$ and carbonate sediments is accordingly $\approx 0.990$. The value of $\alpha_{R/P}$, the fractionation between CO$_2$ and buried organic material is $\approx 1.015$. Combination of these factors as in equation 50 leads to the fractionation between organic and carbonate carbon, $\alpha_{P/Q} \approx 0.975$.

The treatment is also appropriate for isotopic fractionations occurring at an enzymatic reaction site. In this case, the reaction chamber is the microscopic pool of reactants available at the active site of the enzyme, $R$ is the substrate, $P$ is the product, and $Q$ is unutilized substrate (thus $\alpha_{R/Q} \approx 1.000$). Fractionations occurring in networks comprised of multiple systems of this kind have been described by Hayes (2001).

**Irreversible reaction, open system (product accumulated).** Plants exemplify systems of this kind. Carbon and hydrogen are assimilated from infinite supplies of CO$_2$ and H$_2$O and accumulate in the biomass. The problem is trivial, but a particular detail requires emphasis. The fixation of C or H can be represented by

$$R \rightarrow P$$  \hspace{1cm} (51)

The corresponding isotopic relationship can be described by a fractionation factor

$$\alpha_{P/R} = \frac{R_p}{R_R} = \frac{\delta_p - 1}{\delta_R - 1}$$  \hspace{1cm} (52)

The relationship between $\delta_R$ and $\delta_P$ is then described by

$$\delta_P = \alpha_{P/R} \delta_R + \epsilon_{P/R}$$  \hspace{1cm} (53)

This equation is often simplified to this form:

$$\delta_P = \delta_R + \epsilon_{P/R}$$  \hspace{1cm} (54)

For example, to estimate the $\delta$ value of the CO$_2$ that was available to the plant, an experimenter will often refer to "a one-to-one relationship" and subtract $\epsilon_{P/R}$ (typically $\approx -20\%$) from the $\delta$ value of the biomass. For carbon, no serious error will result. The relationship is nearly "one-to-one" (slope $\approx 0.980$).

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**Figure 10.** Comparison of fractionations affecting carbon and hydrogen. In each case, the broken line represents a "one-to-one" approximation and the solid line represents the accurate relationship described by the equation. The approximation is essentially valid for carbon but seriously in error for hydrogen.

For hydrogen, however, this approach leads to disaster. Any experimenter dealing with $\epsilon_{P/R} = -200\%$, a value typical of fractionations affecting deuterium, should remember that the slope of the corresponding relationship must differ significantly from 1 and that equation 53 cannot be replaced by equation 54. This comparison between fractionations affecting carbon and those affecting hydrogen is summarized graphically in Figure 10.
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